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Toward an Improved π-Electron Theory*

GIUSEPPE DEL RE†
RIAS, Baltimore, Maryland
AND
ROBERT G. PARR‡
Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

I. INTRODUCTION

THE problem of refining the simple LCAO–MO or Hückel method for treating complex unsaturated molecules[1] by antisymmetrization and configuration interaction is not new. In addition to treatments based on strictly variational procedures, preceded by mathematical calculations of the necessary integrals,[2] various attempts have been made to formulate semiempirical procedures starting from "configurations".[3-7] The empirical side of these methods lies in the fact that certain integrals are evaluated with the help of experimental data.

Although the methods in question have provided excellent procedures for practical applications,[8,9] all of them start from the idea that any simple LCAO–MO procedure previously used for treating a particular molecule, could, at most, provide a reasonable choice of what Boys calls the predetor functions[10]; it would not eliminate the need of evaluating again the fundamental empirical parameters. For this reason, the procedures so far proposed do not provide complete understanding of the relationship between the results of the simple LCAO–MO method and those obtained from its extensions including antisymmetrization. This situation is not entirely satisfactory.

It is important, therefore, to try to reformulate the explicit inclusion of antisymmetrization and configuration interaction in the LCAO treatment of molecular systems in such a way that light is shed on the relation between the simple theory ignoring detailed electron repulsions and the more complete theory including electron repulsions. That is the main purpose of this paper. Our discussion overlaps in part previous treatments of similar problems,[8,11-13] but several features are new and others are highlighted in a particular way.

II. MATHEMATICAL PRELIMINARIES

The results obtained here will be general, as far as the classes of molecule and types of orbital involved are concerned. One simplifying assumption will be made for electron-repulsion integrals, however; for these integrals we shall use the Mulliken approximation, known to be a good approximation at least for π orbitals.[14]

Let $\mathbf{\Phi} \equiv (\phi_1,\phi_2,\cdots,\phi_N)$ be a system of N atomic orbitals chosen as a basis for an LCAO–MO calculation. We write a general molecular orbital ψ_i in the form

$$\psi_i = \sum\nolimits_\mu c_{\mu i}\phi_\mu \,. \tag{1}$$

Alternatively, in matrix notation, we have

$$\mathbf{\Psi} = \mathbf{\Phi}\mathbf{C} \,. \tag{2}$$

Here $\mathbf{C}$ is the matrix which satisfies the two equations

$$\mathbf{HC} = \mathbf{SCE} \,, \tag{3}$$

$$\mathbf{C}^\dagger\mathbf{SC} = \mathbf{1} \,, \tag{4}$$

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† Present address: Istituto di Fisica Teorica dell'Universita Mostra d'Oltremare, Pad. 19, Napoli, Italy.

‡ Present address: Department of Chemistry, The Johns Hopkins University, Baltimore 18, Maryland.

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where $\mathbf{S}$ is the matrix $(\mathbf{\Phi}^\dagger\mathbf{\Phi})$ the elements of which are

$$S_{\mu\mu} = 1\ , \qquad S_{\mu\nu} = \int \varphi_\mu^* \varphi_\nu d\tau\ . \tag{5}$$

The molecular orbitals ψ_i are orthonormal. The matrix $\mathbf{H}$ is the representation in the basis $\mathbf{\Phi}$ of some appropriate effective operator $\mathcal{H}_{\mathrm{eff}}$. Elucidation of the nature of this operator is an essential problem for us.

For the electron-repulsion integrals which will appear we write

$$(\mu\nu|\rho\sigma) = \int \phi_\mu^*(1)\phi_\rho^*(2)(1/r_{12})\phi_\nu(1)\phi_\sigma(2)d\tau_1 d\tau_2\ , \tag{6}$$

$$(ij|kl) = \int \psi_i^*(1)\psi_k^*(2)(1/r_{12})\psi_j(1)\psi_l(2)d\tau_1 d\tau_2\ . \tag{7}$$

In this notation, Mulliken's approximation is

$$(\mu\nu|\rho\sigma) = \tfrac{1}{4} S_{\mu\nu}S_{\rho\sigma}[(\mu\mu|\rho\rho) + (\nu\nu|\rho\rho) + (\mu\mu|\sigma\sigma) + (\nu\nu|\sigma\sigma)]\ . \tag{8}$$

The stronger zero-differential overlap approximation[15] can be obtained from these (and subsequent) formulas by setting $S_{\mu\nu} = \delta_{\mu\nu}$ and $S_{\rho\sigma} = \delta_{\rho\sigma}$.

We will be dealing with general electron configurations represented in terms of Slater determinants, for example,

$$A \equiv \frac{1}{(n!)^{\frac{1}{2}}} \begin{vmatrix} \lambda_1(1)\lambda_2(1)\cdots\lambda_n(1) \\ \lambda_1(2)\lambda_2(2)\cdots\lambda_n(2) \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ \lambda_1(n)\lambda_2(n)\cdots\lambda_n(n) \end{vmatrix} = \{\lambda_1,\lambda_2,\cdots\lambda_n\}\ , \tag{9}$$

where λ_i denotes a general spin orbital and $i = 1, \cdots, n$, with n the total number of electrons. We shall indicate the various determinants by the letters $A, B, C, \cdots$. The spin orbitals are orthonormal.

The formulas giving the matrix elements of the energy operator will contain integrals of the type $(\lambda_i\lambda_j|\lambda_k\lambda_l)$. [The notation is the same as in Eqs. (6) and (7)]. We may express these integrals in terms of the corresponding integrals over the atomic orbitals, taking into account Eq. (8). In general, one has

$$(\lambda_i\lambda_j'|\lambda_k\lambda_l') = (ij'|kl')\cdot s(i,j')\cdot s(k,l')\ , \tag{10}$$

where a prime denotes that the corresponding spin orbital belongs to a configuration B not necessarily equal to A, and the subscripts i, j, k, l denote molecular orbitals which are the spatial parts of the corresponding spin orbitals λ_i, λ_j, λ_k, λ_l (not necessarily different). The symbol $s(i,j)$ is 1 or 0, according to whether λ_i and λ_j have equal or different spins.

Let us consider now the integral $(ij'|kl')$. We have (supposing that the elements of $\mathbf{C}$ are all real):

$$(ij'|kl') = \textstyle\sum_{\mu\nu\rho\sigma} c_{\mu i}c_{\nu j'}c_{\rho k}c_{\sigma l'}(\mu\nu|\rho\sigma)\ . \tag{11}$$

Introducing Eq. (8), we then obtain

$$\begin{aligned} 4(ij'|kl') = {} & \textstyle\sum_{\mu\nu\rho\sigma} c_{\mu i}c_{\nu j'}c_{\rho k}c_{\sigma l'}S_{\mu\nu}S_{\rho\sigma}(\mu\mu|\rho\rho) \\ & + \textstyle\sum_{\mu\nu\rho\sigma} c_{\mu i}c_{\nu j'}c_{\rho k}c_{\sigma l'}S_{\mu\nu}S_{\rho\sigma}(\mu\mu|\sigma\sigma) \\ & + \textstyle\sum_{\mu\nu\rho\sigma} c_{\mu i}c_{\nu j'}c_{\rho k}c_{\sigma l'}S_{\mu\nu}S_{\rho\sigma}(\nu\nu|\rho\rho) \\ & + \textstyle\sum_{\mu\nu\rho\sigma} c_{\mu i}c_{\nu j'}c_{\rho k}c_{\sigma l'}S_{\mu\nu}S_{\rho\sigma}(\nu\nu|\sigma\sigma)\ . \end{aligned} \tag{12}$$

Since the sums are carried over all the atomic orbitals, we can interchange the corresponding subscripts in the sums, getting

$$\begin{aligned} 4(ij'|kl') = {} & \textstyle\sum_{\mu\nu\rho\sigma} [c_{\mu i}c_{\nu j'}c_{\rho k}c_{\sigma l'}S_{\mu\nu}S_{\rho\sigma} \\ & + c_{\mu i}c_{\nu j'}c_{\sigma k}c_{\rho l'}S_{\mu\nu}S_{\rho\sigma} + c_{\nu i}c_{\mu j'}c_{\rho k}c_{\sigma l'}S_{\mu\nu}S_{\rho\sigma} \\ & + c_{\nu i}c_{\mu j'}c_{\sigma k}c_{\rho l'}S_{\mu\nu}S_{\rho\sigma}](\mu\mu|\rho\rho)\ . \end{aligned} \tag{13}$$

Now, the term in square brackets can be written:

$$(c_{\mu i}c_{\nu j'} + c_{\nu i}c_{\mu j'})S_{\mu\nu}(c_{\rho k}c_{\sigma l'} + c_{\sigma k}c_{\rho l'})S_{\rho\sigma}\ .$$

Therefore, if we define a vector $\mathbf{Q}_{mn'}$, determined by the LCAO coefficients, such that:

$$(\mathbf{Q}_{mn'})_\eta = \tfrac{1}{2} \textstyle\sum_\tau (c_{\tau m}c_{\eta n'} + c_{\eta m}c_{\tau n'})S_{\eta\tau}\ , \tag{14}$$

we obtain finally

$$(ij'|kl') = \mathbf{Q}_{ij'}^\dagger \mathbf{F} \mathbf{Q}_{kl'}\ , \tag{15}$$

where $\mathbf{F}$ is an Nth-order matrix, a matrix of Coulomb-repulsion integrals, whose general element is

$$(\mathbf{F})_{\eta\tau} = (\eta\eta|\tau\tau)\ . \tag{16}$$

The vectors $\mathbf{Q}_{mn'}$ have an important property. Let $\mathbf{1}_N$ be the vector formed by N elements, all equal to 1. Then

$$\begin{aligned} \mathbf{1}_N^\dagger \mathbf{Q}_{mn'} = \mathbf{Q}_{mn'}^\dagger \mathbf{1}_N &= \tfrac{1}{2} \textstyle\sum_{\eta\tau}(c_{\tau m}S_{\tau\eta}c_{\eta n'} + c_{\eta m}S_{\eta\tau}c_{\tau n'}) \\ &= \tfrac{1}{2}[(\mathbf{C}^\dagger\mathbf{SC})_{mn'} + (\mathbf{C}^\dagger\mathbf{SC})_{mn'}] = \delta_{mn'}\ , \end{aligned} \tag{17}$$

where $\delta_{mn'}$ is 0 if the spatial parts of λ_m and λ_n' are different.

III. DERIVATION OF BASIC ENERGY FORMULAS

We now seek the matrix elements $(A|\mathcal{H}|B)$ between two Slater determinants A and B. We let A and B be so ordered that identical spin orbitals bear the same subscripts in both of them. The electronic Hamiltonian $\mathcal{H}$ we take to have the form

$$\mathcal{H} = \textstyle\sum_i \mathcal{H}^{\mathrm{core}}(i) + \tfrac{1}{2} \sum_{ij}' \dfrac{1}{r_{ij}}\ . \tag{18}$$

(The nuclear–nuclear repulsion terms will be added later.) We then find, employing the usual rules,

$$\begin{aligned} (A|\mathcal{H}|B) = {} & \textstyle\sum_k (\lambda_k|\mathcal{H}^{\mathrm{core}}|\lambda_k')\delta_k^{AB} \\ & + \tfrac{1}{2} \textstyle\sum_{kl}'[(\lambda_k\lambda_k'|\lambda_l\lambda_l') - (\lambda_k\lambda_l'|\lambda_l\lambda_k')]\delta_{kl}^{AB}, \end{aligned} \tag{19}$$

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[15] R. G. Parr, J. Chem. Phys. 20, 1499 (1952).

where sums are over occupied orbitals λ_k and λ_l in A, λ'_k and λ'_l in B,

$$(\lambda_k|\mathcal{H}^{\text{core}}|\lambda'_k) = \int \lambda_k^*(1)\mathcal{H}^{\text{core}}(1)\lambda'_k(1)d\tau\,, \qquad (20)$$

and we have introduced the symbol

$$\begin{aligned}\delta_{kl\ldots}^{AB} = \int \lambda_1^*\lambda'_1 d\tau\cdot \int \lambda_2^*\lambda'_2 d\tau \cdots \int \lambda_{k-1}^*\lambda'_{k-1}d\tau \\ \times \int \lambda_{k+1}^*\lambda'_{k+1}d\tau \cdots \int \lambda_{l-1}^*\lambda'_{l-1}d\tau\cdot \int \lambda_{l+1}^*\lambda'_{l+1}d\tau \cdots \\ \times \int \lambda_n^*\lambda'_n d\tau\,, \qquad (\lambda_i\subset A, \lambda'_j \subset B)\,, \qquad (21)\end{aligned}$$

which has only the values 0 or 1. Evidently,

$$\begin{aligned}(\lambda_k|\mathcal{H}^{\text{core}}|\lambda'_k) &= \mathbf{C}_k^\dagger(\mathbf{\Phi}^\dagger\mathcal{H}^{\text{core}}\mathbf{\Phi})\mathbf{C}_{k'}\cdot s(k,k') \\ &= \mathbf{C}_k^\dagger\mathbf{H}^{\text{core}}\mathbf{C}_{k'}\cdot s(k,k')\,. \qquad (22)\end{aligned}$$

From Eqs. (10), (14), and (22) we thus obtain

$$\begin{aligned}(A|\mathcal{H}|B) = \textstyle\sum_k \mathbf{C}_k^\dagger\mathbf{H}^{\text{core}}\mathbf{C}_{k'}\cdot s(k,k')\cdot\delta_k^{AB} \\ + \tfrac{1}{2}\textstyle\sum'_{kl}[\mathbf{Q}_{kk'}^\dagger\mathbf{F}\mathbf{Q}_{ll'}\cdot s(k,k')\cdot s(l,l') \\ - \mathbf{Q}_{kl'}^\dagger\mathbf{F}\mathbf{Q}_{lk'}\cdot s(k,l')\cdot s(l,k')]\delta_{kl}^{AB}\,. \qquad (23)\end{aligned}$$

We observe that two kinds of $\mathbf{Q}_{mn'}$ appear in the second sum of Eq. (23). The second term of the sum is formed solely by vectors deriving from different molecular orbitals. In fact, it is formed (due to the special ordering of the configurations) by different spin orbitals: The presence of the factors $s(k,l')$ and $s(l,k')$ makes the term vanish if the corresponding spin orbitals have the same spatial parts. Now vectors $\mathbf{Q}_{mn'}$ deriving from molecular orbitals essentially different have a vanishing sum of their elements: We intend to introduce certain new vectors $\tilde{\mathbf{Q}}_{mn'}$ such that this property be common to all of them. These vectors are [see Eq. (17)]

$$\tilde{\mathbf{Q}}_{mn'} = \mathbf{Q}_{mn'} - (\delta_{mn'}/N)\mathbf{1}_N\,. \qquad (24)$$

The second term of the argument of the second sum in Eq. (23) can be rewritten in terms of the $\tilde{\mathbf{Q}}_{mn'}$ without any other change. As for the first term, it can be rewritten

$$\begin{aligned}\mathbf{Q}_{kk'}^\dagger\mathbf{F}\mathbf{Q}_{ll'} &= \left(\tilde{\mathbf{Q}}_{kk'}^\dagger + \frac{\delta_{kk'}}{N}\mathbf{1}_N^\dagger\right)\mathbf{F}\left(\tilde{\mathbf{Q}}_{ll'} + \frac{\delta_{ll'}}{N}\mathbf{1}_N\right) \\ &= \tilde{\mathbf{Q}}_{kk'}\mathbf{F}\tilde{\mathbf{Q}}_{ll'} + \frac{\delta_{kk'}}{N}\mathbf{1}_N^\dagger\mathbf{F}\tilde{\mathbf{Q}}_{ll'} + \tilde{\mathbf{Q}}_{kk'}\mathbf{F}\mathbf{1}_N\frac{\delta_{ll'}}{N} \\ &+ \frac{\delta_{kk'}}{N}\mathbf{1}_N^\dagger\mathbf{F}\mathbf{1}_N\frac{\delta_{ll'}}{N}\,. \qquad (25)\end{aligned}$$

Now, according to Eq. (21),

$$\delta_m^{AB} = \delta_{mn'}^{AB}\cdot s(n,n')\cdot\delta_{nn'}\,. \qquad (26)$$

Therefore,

$$\begin{aligned}&\tfrac{1}{2}\textstyle\sum'_{kl}\tilde{\mathbf{Q}}_{kk'}^\dagger\mathbf{F}\mathbf{1}_N\dfrac{1}{N}\delta_{ll'}\cdot s(k,k')\cdot s(l,l')\cdot\delta_{kl}^{AB} \\ &= \tfrac{1}{2}\textstyle\sum'_{kl}\tilde{\mathbf{Q}}_{kk'}^\dagger\mathbf{F}\mathbf{1}_N\dfrac{1}{N}\cdot s(k,k')\cdot\delta_k^{AB} \\ &= \dfrac{n-1}{2N}\textstyle\sum_k\tilde{\mathbf{Q}}_{kk'}^\dagger\mathbf{F}\mathbf{1}_N\cdot s(k,k')\cdot\delta_k^{AB} \\ &= \dfrac{n-1}{2N}\textstyle\sum_k\tilde{\mathbf{Q}}_{kk'}^\dagger\mathbf{F}\mathbf{1}_N\cdot s(k,k')\cdot\delta_k^{AB} \\ &- \dfrac{n(n-1)}{2N^2}\mathbf{1}_N^\dagger\mathbf{F}\mathbf{1}_N\delta^{AB}\,. \qquad (27)\end{aligned}$$

The same procedure also holds for the term $(\delta_{kk'}/N)\times\mathbf{1}_N^\dagger\mathbf{F}\tilde{\mathbf{Q}}_{ll'}$ of Eq. (25), which gives the same results, because it is a real scalar which can be transposed without changing its value and because k and l can be interchanged in the sum. Finally,

$$\begin{aligned}&\tfrac{1}{2}\textstyle\sum'_{kl}\dfrac{\delta_{kk'}}{N}\mathbf{1}_N^\dagger\mathbf{F}\mathbf{1}_N\dfrac{\delta_{ll}}{N}\cdot s(k,k')\cdot s(l,l')\cdot\delta_k^{AB} \\ &= \dfrac{1}{2N^2}\textstyle\sum'_{kl}\mathbf{1}_N^\dagger\mathbf{F}\mathbf{1}_N\delta^{AB} = \dfrac{n(n-1)}{2N^2}\mathbf{1}_N^\dagger\mathbf{F}\mathbf{1}_N\delta^{AB}\,. \qquad (28)\end{aligned}$$

Let us now notice that

$$\begin{aligned}\mathbf{Q}_{kk'}^\dagger\mathbf{F}\mathbf{1}_N &= \tfrac{1}{2}\textstyle\sum_{\mu\nu\rho}[c_{\mu k}c_{\nu k'}S_{\mu\nu}(\mu\mu|\rho\rho) + c_{\nu k}c_{\mu k'}S_{\mu\nu}(\mu\mu|\rho\rho)] \\ &= \tfrac{1}{2}\textstyle\sum_{\mu\nu}\{c_{\mu k}S_{\mu\nu}\textstyle\sum_\rho[(\mu\mu|\rho\rho) + (\nu\nu|\rho\rho)]c_{\nu k'}\} \\ &= \mathbf{C}_k^\dagger(\mathbf{SJ}+\mathbf{JS})\mathbf{C}_{k'} = \mathbf{C}_k^\dagger\mathbf{K}\mathbf{C}_{k'}\,, \qquad (29)\end{aligned}$$

where

$$(\mathbf{J})_{\eta\tau} = \tfrac{1}{2}\textstyle\sum_\rho(\eta\tau|\rho\rho)\delta_{\eta\tau}\,, \qquad (30)$$

and also, under Mulliken's approximation Eq. (8),

$$\begin{aligned}(\mathbf{K})_{\mu\nu} &= \textstyle\sum_\rho\{\tfrac{1}{2}S_{\mu\nu}[(\mu\mu|\rho\rho) + (\nu\nu|\rho\rho)]\} \\ &= \textstyle\sum_\rho(\rho\rho|\mu\nu)\,. \qquad (31)\end{aligned}$$

Upon substituting Eq. (25) into Eq. (23) and taking into account Eqs. (28) and (29), we obtain

$$\begin{aligned}(A|\mathcal{H}|B) = -\frac{n(n-1)}{2N^2}\mathbf{1}_N^\dagger\mathbf{F}\mathbf{1}_N\delta^{AB} \\ + \textstyle\sum_k\mathbf{C}_k^\dagger\left(\mathbf{H}^{\text{core}} + \dfrac{n-1}{N}\mathbf{K}\right)\mathbf{C}_{k'}\cdot s(k,k')\delta_k^{AB} \\ + \tfrac{1}{2}\textstyle\sum'_{kl}[\tilde{\mathbf{Q}}_{kk'}^\dagger\mathbf{F}\tilde{\mathbf{Q}}_{ll'}\cdot s(k,k')\cdot s(l,l') \\ - \tilde{\mathbf{Q}}_{kl'}^\dagger\mathbf{F}\tilde{\mathbf{Q}}_{lk'}\cdot s(k,l')\cdot s(l,k')]\delta_{kl'}^{AB}\,. \qquad (32)\end{aligned}$$

This is our final formula for the matrix elements of the electronic Hamiltonian operator.

The molecular core—sigma electrons and nuclei—has an energy which must be included in the total energy of each molecular state. The atoms in the core generally bear one or more positive charges, the

Coulomb repulsions between which are long range effects which will vary substantially from molecule to molecule. To obtain a formula which will contain all essential long-range effects we separate out these Coulomb terms

$$E_{\text{core}} = E_0^{\text{core}} + E_{\text{Coulombic}}^{\text{core}} \tag{33}$$

and take a new Hamiltonian,

$$\mathcal{H}^{\text{tot}} = \mathcal{H} + E_{\text{Coulombic}}^{\text{core}} . \tag{34}$$

Further, we note that the Coulombic terms are not point-charge repulsions, but repulsions between orbital-like positive "holes" in neutral charge clouds[16]:

$$E_{\text{Coulombic}}^{\text{core}} = \tfrac{1}{2} \textstyle\sum_{\sigma\rho}^{*\prime} (\sigma\sigma|\rho\rho) . \tag{35}$$

Here the double sum is over all orbitals which when filled with one electron each make all atoms neutral, essentially spherical entities, and the sum excludes repulsion of each orbital with itself.

We can now write the matrix elements of $\mathcal{H}^{\text{tot}}$ as the sum of three terms:

$$(A|\mathcal{H}^{\text{tot}}|B) = (\text{Term I}) + (\text{Term II}) + (\text{Term III}) , \tag{36}$$

where

$$\text{Term I} = E_{\text{Coulombic}}^{\text{core}} \delta^{\text{AB}} - \frac{n(n-1)}{2N^2} \mathbf{1}_{\text{N}}^{\dagger} \mathbf{F} \mathbf{1}_{\text{N}} \delta^{\text{AB}} , \tag{37}$$

$$\begin{aligned} \text{Term II} = {} & \textstyle\sum_k \mathbf{C}_k^{\dagger} \left(\mathbf{H}^{\text{core}} + \dfrac{n-1}{N} \mathbf{K} \right) \mathbf{C}_{k'} \\ & \times s(k,k') \delta_k^{\text{AB}} , \end{aligned} \tag{38}$$

$$\begin{aligned} \text{Term III} = {} & \tfrac{1}{2} \textstyle\sum_{kl}^{\prime} [\tilde{\mathbf{Q}}_{kk'}^{\dagger} \mathbf{F} \tilde{\mathbf{Q}}_{ll'} \cdot s(k,k') \cdot s(l,l') \\ & - \tilde{\mathbf{Q}}_{kl'}^{\dagger} \mathbf{F} \tilde{\mathbf{Q}}_{lk'} \cdot s(k,l') \cdot s(l,k')] \delta_{kl}^{\text{AB}} . \end{aligned} \tag{39}$$

These terms will be separately analyzed in the next section.

IV. ANALYSIS OF BASIC ENERGY FORMULAS

In Eq. (36), Term I corresponds to a constant operator, independent of the molecular orbitals, and it is present only in the diagonal elements of the energy matrix; it plays the role of a zero-point correction. Term II is a Hückel-like term that we will want to look at closely. Term III is a more complex correction, without analogy in the Hückel scheme.

Discussion of Term I

To get a feeling for Term I, let us evaluate the mean repulsion between two electrons distributed at random among the various atomic orbitals of the basis. This repulsion would be given by

$$R_2 = \frac{1}{N^2} \textstyle\sum_{\sigma\rho} (\sigma\sigma|\rho\rho) . \tag{40}$$

Extending the argument, for the average repulsion for n electrons we would have

$$R_n = \frac{n(n-1)}{2N^2} \textstyle\sum_{\sigma\rho} (\sigma\sigma|\rho\rho) = \dfrac{n(n-1)}{2N^2} \mathbf{1}_{\text{N}}^{\dagger} \mathbf{F} \mathbf{1}_{\text{N}} . \tag{41}$$

This shows that the constant Term I is a sort of average electron–electron repulsion *subtracted* from the nuclear–nuclear repulsion.

For neutral molecules we may expect considerable cancellation between the two parts of Term I. For simplicity consider the case $n = N$, one π orbital per nucleus, and a neutral molecule. Then we would have, from Eqs. (35), (37), and (41), for $A = B$,

$$\begin{aligned} \text{Term I} = {} & -\frac{1}{2N} [(N-1) \textstyle\sum_{\sigma} (\sigma\sigma|\sigma\sigma) \\ & - \textstyle\sum_{\sigma\rho}^{\prime} (\sigma\sigma|\rho\rho)] \end{aligned} \tag{42}$$

[special case only] .

This is a simple sum of differences of electronic-repulsion integrals.

A discussion of the other two terms will allow us to further clarify the meaning of Term I. We remark finally at this point that the term in question depends both upon N and n. If, with the number of electrons the same, N is increased (*i.e.*, if the basis comes closer and closer to a complete set), Term I goes over into a pure nuclear–nuclear repulsion term.

Discussion of Term II

If only Term II of Eq. (36) were present, we would have a simple Hückel theory, with the operator $\mathcal{H}_{\text{eff}}$ of Eq. (3) given in matrix form by

$$\mathbf{H}_{\text{eff}} = \mathbf{H}^{\text{core}} + [(n-1)/N] \mathbf{K} . \tag{43}$$

In operator form we would have

$$\mathcal{H}_{\text{eff}} = \mathcal{H}^{\text{core}} + [(n-1)/N] \mathcal{R} , \tag{44}$$

where in turn $\mathcal{R}$ is the Coulomb field generated by N valence electrons of the system [see Eq. (31)]:

$$\mathcal{R} = \textstyle\sum_{\rho} \displaystyle\int \phi_{\rho}^{*}(2) \phi_{\rho}(2) (1/r_{12}) d\tau_2 . \tag{45}$$

Let us consider the potential energy term in $\mathcal{H}_{\text{eff}}$. Let a denote a single atom which contributes N_a orbitals to the atomic orbital system, ($\sum_a N_a = N$). In

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[16] R. G. Parr and R. Pariser, J. Chem. Phys. **23**, 711 (1955).

a central field approximation, the corresponding potential energy term is given by

$$U_a^*(1) = U_a^{\text{core}}(1) + \sum_{\rho_a=1}^{N_a} n_{\rho_a} \int \phi_{\rho_a}^*(2)\phi_{\rho_a}(2)(1/r_{12})d\tau_2 , \tag{46}$$

where n_{ρ_a} denotes the number of electrons belonging to ϕ_{ρ_a}. We now suppose that the n electrons of the system under study are distributed uniformly among all the orbitals. Since we are considering one electron in the average field of all the others, the electrons we are interested in here are $n - 1$. The mean occupation number of a given orbital will thus be $(n - 1)/N$, and Eq. (46) becomes

$$\begin{aligned} U_a^*(1) = {} & U_a^{\text{core}}(1) \\ & + \sum_{\rho_a=1}^{N_a} \frac{n-1}{N} \int \phi_{\rho_a}^*(2)\varphi_{\rho_a}(2)(1/r_{12})d\tau_2 . \end{aligned} \tag{47}$$

Equation (47) may be regarded as a generalization of a well-known Goeppert-Mayer and Sklar formula,[2] to the general case of atoms which furnish any number of electrons (less than $2N_a$) and any number of orbitals. It leads to the expression

$$\mathcal{H}_{\text{eff}}(1) = \mathcal{T}(1) + \textstyle\sum_a U_a^*(1) . \tag{48}$$

It is worth noting that Eq. (48) can be given a very simple interpretation: The effective Hamiltonian is still a core Hamiltonian: it corresponds to a core including all the electrons minus one, wherein the various atoms are assigned equal fractions per orbital of the electrons of the system. With this definition, the effective Hamiltonian is fictitious not only because of its one-electron nature, but also because it relates to atoms in which nonintegral numbers of electrons are present.

The potential $U_a^*(1)$ tends to that of a neutral atom when

$$|n - N - 1| \ll N . \tag{49}$$

This in general implies that N should be very large and the average number of electrons per atomic orbital should be close to one. It must also be noted that the expression "neutral atom" in this context signifies an atom whose valence orbitals are each singly occupied; the "neutral atom" corresponding to nitrogen in a system like the π system of pyrrole is actually the positive nitrogen ion.

A few examples showing the values the factor $(n - 1)/N$ can take may be instructive. Let n_a be the electrons actually shared by atom a, and N_a be the orbitals which belong to it; the defect of electrons formally assigned to a by Eq. (47) with respect to its nonbonded state is then:

$$d_a = n_a - N_a \frac{n-1}{N} . \tag{50}$$

We call d_a the "core charge" of atom a. We then consider as an example the π systems of compounds formed by condensed five-membered rings with one heteroatom sharing an electron pair per ring (e.g., pyrrolopyrroles). In this case $(n - N - 1) = m - 1$, where m is the number of rings, and $N = 2 + 3m$. Here we have two types of atoms: C, with $n_c = 1$, and X (in pyrroles X is nitrogen) where $n_x = 2$. Values of d are as follows:

m	1	2	3	4	5	6	∞
d_c	0	$-\frac{1}{8}$	$-\frac{2}{11}$	$-\frac{3}{14}$	$-\frac{4}{17}$	$-\frac{1}{4}$	$-\frac{1}{3}$
d_x	$+1$	$+\frac{7}{8}$	$+\frac{9}{11}$	$+\frac{11}{14}$	$+\frac{13}{17}$	$+\frac{3}{4}$	$+\frac{2}{3}$

The core charges shown here are fairly high, and they tend to further increase in magnitude when $m \to \infty$. It is not necessary to build a table to show that, on the contrary, if the number of heteroatoms with a lone pair is kept constant, the core charge tends to zero, when the number of atoms increases.

Ruedenberg[12] has remarked that in hydrocarbons an electron tends to see the atoms as essentially neutral atoms. The preceding discussion clearly shows that Eq. (48) gives a mathematical formulation of this remark and that the remark definitely does not hold true for complicated heterocyclics.

If the identification of the Hamiltonian of Eq. (44) or Eq. (48) with the Hückel Hamiltonian is accepted, one sees that the validity of a Hückel procedure is contingent upon the condition of Eq. (49). This, in general, holds for rather large values of N, except in the case of heterocyclics like those treated above.

Let us now go back to Term I. The physical interpretation leading to Eq. (48) describes each electron in the field of the other $n - 1$ electrons distributed in amounts $(n - 1)/N$ among the various atomic orbitals. If the electron in question were localized on the σ-th orbital, we would have a repulsion $[(n - 1)/N]\sum_\rho (\rho\rho|\sigma\sigma)$. But each electron is supposed to be distributed in equal fractions over all the N atomic orbitals, for which the average repulsion will be

$$\bar{R}' = \frac{n-1}{N^2} \textstyle\sum_{\rho\sigma} (\rho\rho|\sigma\sigma) . \tag{51}$$

This shows how electron repulsion is taken into account in the $\mathcal{H}_{\text{eff}}$ of Eq. (48). It can be seen that this interpretation is correct by considering that $\tilde{\mathbf{Q}}_{mn}$ is defined by Eq. (24) and is a net charge vector (*vide infra*). Now when the energy of a configuration is calculated, the expectation values of $\mathcal{H}_{\text{eff}}$ are summed over n electrons. The total repulsion energy taken into account in this way is [see Eq. (41)]

$$n\bar{R}' = 2R_n . \tag{52}$$

This shows that the term $-R_n$ that enters Term I is actually only a correction relating to a double sum similar to the correction that is introduced when, in the Hartree–Fock method, the sum of the orbital energies is to be used for evaluating the total energy.

This analysis shows that together the first two terms of Eq. (36) take into account the electron repulsion as far as it can be treated as an average repulsion relating to all the possible equivalent distributions of the n electrons over the N atomic orbitals. Term I could in principle be combined with Term II.[13] However, it may be useful to keep them separate. If we assume that Term III represents only a perturbation on the energy, it follows that the charge distributions (and hence the dipole moments) of molecules are essentially determined by $\mathcal{H}_{\text{eff}}$.

Discussion of Term III

Term III of Eq. (36) is a correction which cannot be related directly to an appropriate operator, because of the nature of the vectors $\tilde{\mathbf{Q}}_{mn'}$.

In general, it is not possible to give an intuitive interpretation of all of the vectors $\tilde{\mathbf{Q}}_{mn'}$, because they are expressions which contain the coefficients of different molecular orbitals, and, hence, are related as much to the particular mathematical nature of the orbital approximation as to physical facts. However, when the orbitals to which the subscripts m and n' refer are the same, it is possible to use a well-known interpretation of the elements of $\tilde{\mathbf{Q}}_{mn'}$: they are the net charge of the given molecular orbital. This interpretation is important, for instance, when the fundamental state of a system is described by a single configuration. Then, of the two terms which make up the argument of the double sum, the first one is classically interpretable as the contribution to the interaction energy between the electrons resulting from the fact that the latter are not uniformly distributed over the molecule; the second term is the well-known exchange term which represents essentially an additional correction related to the fact that a Slater determinant distributes each electron with different spins over different orbitals, so that the interaction, even classically, is no longer given only by the repulsions contained in the first part of the sum under study.

As to the quantitative importance of Term III, if the values of the integrals were the same, the correction terms would be the smaller the more uniform the charge distribution of each molecular orbital. Consequently, we can conclude that a system in which the atoms and bonds are similar to each other will usually be rather well described by the Hückel method. This is due also to the fact that, if the net charge on an atom is quite high for a given molecular orbital, it will usually happen that the other charges are rather small. In other words, products of elements of the $\tilde{\mathbf{Q}}$ vectors are essentially second-order corrections withrespect to the charges.

On the other hand, it must be noted that the effect of Term III is introduction of some long-range effects. This is because the elements of the matrix **F** cannot be treated by simple nearest-neighbor approximation, and, hence, they can sometimes produce important contributions coming from atoms quite far from each other. An interesting consequence of this is that "localized" bonds in the sense of the Hückel method may in some cases interact quite strongly when Term III is taken into account.

A further elucidation of Term III would bring in effective electronegativities and electronegativity differences.[16,17]

V. NEAREST NEIGHBOR APPROXIMATION

We must now examine the possibility of introducing a nearest neighbor approximation into Eq. (36), for if this could be done the problem of evaluating empirically all integrals could be made quite simple.

As far as the effective Hamiltonian $\mathcal{H}_{\text{eff}}$ of Eq. (48) is concerned, since the potential terms in it are quite close to those of a neutral atom, it gives rise mainly to short-range forces, and, hence, it can be more or less easily reduced to a nearest-neighbor approximation. We should add, however, that the foregoing analysis shows also that this approximation is not very satisfactory when one or more atomic orbitals share with the electron system under study more than one electron, because the corresponding atoms appear essentially as ions in the system.

On the other hand, there is not much hope that the nearest neighbor approximation can actually be used as far as Term III is concerned, notwithstanding some results obtained by Murrell and Salem.[18] As far as the matrix **F** is concerned, those authors indicated

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[17] R. G. Parr, J. Chem. Phys. **33**, 1184 (1960).

[18] J. N. Murrell and L. Salem, J. Chem. Phys. **34**, 1914 (1961).

that some sort of nearest-neighbor approximation was possible, at least for the π systems of hydrocarbons. In order to examine the problem in general, we reformulate their basic theorem on the basis of Eq. (36).

We know that $\sum_\mu (\tilde{\mathbf{Q}}_{mn'})_\mu = 0$. Therefore, if we add to $\mathbf{F}$ two matrices of the same order N resulting from the products of two diagonal matrices $\mathbf{w}$ and $\mathbf{v}$ by the matrix $\mathbf{1}_{NN}$ whose elements are all equal to one, the product $\tilde{\mathbf{Q}}^\dagger_{ij'}\mathbf{F}\tilde{\mathbf{Q}}_{lk'}$ remains the same. In fact, let

$$\mathbf{F}' = \mathbf{F} + \mathbf{w}\mathbf{1}_{NN} + \mathbf{1}_{NN}\mathbf{v}\,. \tag{53}$$

From Eqs. (17) and (24) we find:

$$\tilde{\mathbf{Q}}^\dagger_{mn'}\cdot\mathbf{1}_{NN} = 0\,; \qquad \mathbf{1}_{NN}\tilde{\mathbf{Q}}_{mn'} = 0\,. \tag{54}$$

Therefore,

$$\tilde{\mathbf{Q}}^\dagger_{ij'}\mathbf{F}'\tilde{\mathbf{Q}}_{lk'} = \tilde{\mathbf{Q}}^\dagger_{ij'}\mathbf{F}\tilde{\mathbf{Q}}_{lk'}\,. \tag{55}$$

Let us now build the matrix

$$[\mathbf{A}]_{\mu\nu} = \tfrac{1}{2}\,(F_{\mu\mu} + F_{\nu\nu})\,. \tag{56}$$

This matrix is of the type $\mathbf{w}\mathbf{1}_{NN} + \mathbf{1}_{NN}\mathbf{v}$, and therefore $\mathbf{F}' = \mathbf{F} - \mathbf{A}$ satisfies Eq. (55). Now,

$$(\mathbf{F}')_{\mu\nu} = F_{\mu\nu} - \tfrac{1}{2}\,F_{\mu\mu} - \tfrac{1}{2}\,F_{\nu\nu} = (\mathbf{F}')_{\nu\mu}\,. \tag{57}$$

Therefore, it is evident that the matrix $\mathbf{F}$ can be replaced by a matrix $\mathbf{F}'$ defined by Eq. (57), where all the elements can be expressed as sums of differences between electron repulsion integrals: these differences can, in fact, be made to correspond to nearest neighbors, next nearest neighbors, etc., but this has to be done on the basis of the particular topology of each individual molecule. In addition, one wonders whether the argument given by Murrell and Salem to support the conclusion that, when differences are used, the differences relating to non-nearest neighbors can be neglected, also holds when sums of such differences are considered. Ruedenberg has come to similar conclusions.[12]

Although these remarks do not prove that a nearest-neighbor approximation is necessarily impossible, they show that it cannot be introduced in a direct and general fashion. Moreover, it seems clear that when the charges of atoms far apart are disparate and not negligible, the effect of Term III is definitely to remove the justification for a nearest neighbor approximation.

VI. CONCLUSIONS

For those cases where the factor $(n - N - 1)/N$ is small, we have seen that $\mathcal{H}_{\text{eff}}$ does satisfy the condition which is implied by the Hückel method, namely, it gives rise essentially only to short range forces[12] and hence parameters reasonably constant from molecule to molecule. It is also clear that dipole moments may be good physical quantities for determining empirically the matrix elements of $\mathcal{H}_{\text{eff}}$. Thus $\mathcal{H}_{\text{eff}}$ can be considered sufficient for a satisfactory treatment of a molecular problem under the condition that the energy be calculated taking into account at least Term I of Eq. (36). The latter depends essentially on the nature of the atomic orbitals and upon the geometry of the molecule; it can be included if it is so wished. In general, the energies obtained from $\mathcal{H}_{\text{eff}}$ alone will be comparable to each other under the usual condition that they be referred to similar frameworks, or that there be differences where the framework effects somehow cancel out.

It thus is possible to define an atomic Hamiltonian which is neither the core Hamiltonian nor that of a neutral atom, but an intermediate one, which comes close to the latter when the number of electrons is very close to that of atomic orbitals and the latter is large, and it is possible to identify this Hamiltonian with the Hückel Hamiltonian of simple LCAO–MO calculations in the sense that its use is equivalent to neglecting only the contribution to the electron repulsion due to the details of the electron distribution in the molecular system.[13]

If this identification of $\mathcal{H}_{\text{eff}}$ with a Hückel Hamiltonian is made, a better interpretation of the validity and limitations of the nearest neighbor approximation in the Hückel method becomes possible; in addition, it is possible to define the correction to the sum of the orbital energies that is necessary in order to obtain the correct total energy. This correction does not depend upon the coefficients of the molecular orbitals obtained from $\mathcal{H}_{\text{eff}}$; it can be considered as contribution to the "framework" energy of the system under study.[12]

In the scheme obtained here, and within the limits of any physical interpretation of exchange terms, the energy obtained from a Hückel scheme differs from the actual energy because of the non-uniformity of the electron distribution in each orbital. This difference, represented by Term III of Eq. (36), can be given an interpretation in terms of net charges and "transition" charges, so that it is possible to analyze better what systems may be expected to give reasonable results when treated according to the Hückel scheme, and what systems are, on the contrary, very much affected by the more accurate treatment, and in particular by the inclusion of long-range effects.

Although it may have some advantages from the computational point of view, Eq. (36) is but a different way of writing well-known formulas. The most significant aspect of the results obtained here are that they may provide a formal link between the Hückel method and the inclusion of antisymmetrization in the LCAO scheme, thus making the analysis of the relationship between the two easier, and, in particular, providing the possibility of transferring whatever physical interpretations may be given to the results of the simple method to those of a more refined calculation. It may also be noticed that our treatment has been carried out without any limitation to special classes of molecular systems (with the possible exception of those for which Mulliken's approximation does not hold). It therefore may help to make a little clearer the problems involved in the extension of methods primarily conceived and tested for the π-systems of hydrocarbons to electronic systems involving different species of atoms and atomic orbitals.

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Intermolecular Forces

A. Dalgarno*
Geophysics Corporation of America, Bedford, Massachusetts

1. INTRODUCTION

THE concept of an intermolecular force between a pair of particles has been of great value in our nuderstanding of a wide range of phenomena and considerable attention has been given in recent years to the problem of deriving the intermolecular forces appropriate to specific atomic and molecular systems. The subject of intermolecular forces was reviewed in 1960 by Buckingham[1] for neutral systems and by Dalgarno[2] for ionic systems, and this review is concerned mainly with subsequent developments.

2. SEMIEMPIRICAL PROCEDURES

It is appropriate to begin with a description of semiempirical procedures since their application has provided most of our detailed knowledge of intermolecular forces. There are two procedures, one of which employs data on transport coefficients and scattering and the other of which employs spectroscopic data.

2.1 Transport Coefficients

The mathematical theory of nonuniform spherically symmetric gases, developed by Chapman and Enskog,[3] reduces the prediction of transport phenomena to the calculation of scattering cross sections

$$Q_l(v) = 2\pi \int_0^\pi I(v,\theta)(1 - \cos^l\theta) \sin\theta d\theta \,, \qquad (1)$$

where θ is the angle of scattering, v is the relative velocity of the colliding particles, $I(v,\theta)$ is the differential cross section, and l is a positive integer. To a first approximation, the coefficient of diffusion is determined by $Q_1(v)$ and the coefficients of viscosity and thermal conductivity by $Q_2(v)$, while the coefficient of thermal diffusion depends upon $Q_1(v)$ and $Q_2(v)$. Explicit expressions for these various transport coefficients may be derived from formulas given in the treatise of Hirschfelder, Curtiss, and Bird.[3]

If the interaction potential $V(R)$, R being the separation of the colliding particles, is known, $I(v,\theta)$ can be calculated. Because the factor $(1 - \cos^l\theta)$ in the integrand of (1) suppresses the contribution from small-angle scattering, a classical description of the scattering is usually sufficiently accurate. According to it, the cross sections may be written

$$Q_l(v) = 2\pi \int_0^\infty (1 - \cos^l\theta) p dp \,, \qquad (2)$$

where

$$\theta(p) = \pi - 2p \int_{R_m}^\infty \frac{dR/R^2}{\left[1 - \frac{p^2}{R^2} - \frac{2V(R)}{\mu v^2}\right]^{\frac{1}{2}}} \,, \qquad (3)$$

p being the impact parameter, μ the reduced mass, and R_m the classical distance of closest approach.

For light elements at low temperatures, it may be necessary to use a quantal description of the scattering. According to it

$$Q_1(v) = \frac{4\pi}{k^2} \sum_{s=0}^\infty (s+1) \sin^2(\eta_{s+1} - \eta_s) \qquad (4)$$

and

$$Q_2(v) = \frac{4\pi}{k^2} \sum_{s=0}^\infty \frac{(s+1)(s+2)}{(2s+3)} \sin^2(\eta_{s+2} - \eta_s) \,, \qquad (5)$$

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* On leave of absence from Department of Applied Mathematics, Queen's University of Belfast, Northern Ireland.

[1] R. A. Buckingham, Planetary Space Sci. **3**, 205 (1961).

[2] A. Dalgarno, Planetary Space Sci. **3**, 217 (1961).

[3] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).